Mitigation: The FEI project

Bertrand Matthäus¹, Anne Freudenstein¹, Frank Pudel², Tim Rudolph², Knut Franke³ und Ulf Strijowski³

¹ Max Rubner-Institut, Detmold
² Pilot Pflanzenöltechnologie Magdeburg e.V., Magdeburg
³ Deutsches Institut für Lebensmitteltechnik e.V., Quakenbrück

As it is not just individual products or products of individual manufacturers that are affected by the problems surrounding 3-MCPD fatty acid esters, alternative techniques must, in principle, be developed for the production of refined fats and oils.
Investigations on the formation of 3-monochloropropane-1,2-diol fatty acid esters (3-MCPD esters) in vegetable oils and development of minimization strategies

Aims

- **Clarification** of the relationship between formation of 3-MCPD esters and related compounds, process conditions and composition of involved components
- **Recommendations** for the definition of processes resulting in mitigation of 3-MCPD esters and related compounds without impairing product quality
- **Removal** of 3-MCPD esters and related compounds from the refined product
- **Development of a direct method** based on SIV A with LC-MS for the quantification of the esters

Max Rubner-Institut, Münster (MRI)

Pilot Pflanzenöl Magdeburg e.V. (PPM)

Deutsche Forschungsanstalt für Lebensmittelchemie (DFA)

Deutsches Institut für Lebensmitteltechnik e.V.
Mitigation strategy

Raw material (removal of precursors)

- soil?
- fertilizer?
- genotype?
- Technique of harvest?
- Time between ripeness and processing?

Refining (Changing of the process)

- Influence of degumming, neutralization, bleaching and deodorization
- Introduction of additionals processing steps

Product (Removal of the esters)

- Effect of different organic and inorganic adsorbens materials with simultaneous maintenance of the product quality
Capability of crude oils to form 3-MCPD esters and related compounds after heating (240 °C, 2h)

Graph showing the MCPD-FE and related compounds [mg/kg] for various oils and fats, including:
- Avocado oil
- Palm oil
- Olive oil
- Rapeseed oil
- Corn oil
- Soybean oil
- Sunflower oil
- Coconut oil
- Palm kernel fat

Regions A to E and countries such as Malaysia, Columbia, Ghana, Indonesia are also shown on the graph.
Correlation between content of diacylglycerols and 3-MCPD esters and related compounds in different oils

![Graph showing the correlation between content of diacylglycerols and 3-MCPD esters and related compounds in different oils.](image)
Influence of polar compounds and diacylglycerols on the formation of 3-MCPD esters and related compounds

- Diacylglycerol
- Polar compounds from palm oil

R² = 0.9092
R² = 0.9259
Influence of chlorine containing compounds on the formation of 3-MCPD esters and related compounds

Chloride added as NaCl

Chloride added as TBAC

R² = 0.9252

R² = 0.9799
Mitigation strategy

- Raw material (removal of precursors)
  - soil?
  - fertilizer?
  - genotype?
  - Technique of harvest?
  - Time between ripeness and processing?

- Refining (Changing of the process)
  - Influence of degumming, neutralization, bleaching and deodorization
  - Introduction of additional processing steps

- Product (Removal of the esters)
  - Effect of different organic and inorganic adsorbens materials with simultaneous maintenance of the product quality
Impact of refining on the formation of 3-MCPD esters and related compounds

Degumming

- crude palm oil 240°C, 2h
- crude palm oil KOH, 240°C, 2h
- crude palm oil NaOH, 240°C, 2h

Neutralisation

- crude palm oil 240°C, 2h
- crude palm oil KOH, 240°C, 2h
- crude palm oil NaOH, 240°C, 2h

Bleaching

- crude palm oil 240°C, 2h
- crude palm oil 1% Tonsil 4191 FF, 240°C, 2h

Refined oil

- crude palm oil
- crude palm oil 20% water, 240°C, 2h
- crude palm oil 5% water + 0.12% phosphoric acid, 240°C, 2h
- crude palm oil 5% water + 0.3% citric acid, 240°C, 2h


ILSI Workshop on MCPD and Glycidyl esters in Food Products, 09 -10 November 2011, Brussels
Influence of temperature and time of washing

Simulation of deodorisation by heating at 240 °C for 120 min

ILSI Workshop on MCPD and Glycidyl esters in Food Products, 09 - 10 November 2011, Brussels
Addition of diacetin during deodorisation

- 47%
- 30%
- 49%
Zeolithe material during deodorisation

Crude palm oil; deodorisation: 250 °C 2 h
Comparison between one and two step deodorisation

Starting material: Palm oil, bleached with 1.5 % Tonsil Optimum 215
Comparison between short path distillation and industrial deodorisation

<table>
<thead>
<tr>
<th></th>
<th>Content [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red palm oil after short path destillation</td>
<td>2</td>
</tr>
<tr>
<td>Industrial deodorised palm oil</td>
<td>11</td>
</tr>
</tbody>
</table>

3-MCPD esters and related compounds

3-MCPD esters
Mitigation strategy

- Refining (Changing of the process)
  - Raw material (removal of precursors)
    - soil?
    - fertilizer?
    - genotype?
    - Technique of harvest?
    - Time between ripeness and processing?
  - Influence of degumming, neutralization, bleaching and deodorization
  - Introduction of additionals processing steps

- Product (Removal of the esters)
  - Effect of different organic and inorganic adsorbens materials with simultaneous maintenance of the product quality
Reduction of 3-MCPD-FE and related compounds after refining

**Background:**

- Differences in polarity of 3-MCPD-FE in comparison to triacylglycerols can be used for separation
- Procedure comparable to the removal of polar compounds from used frying fats for improving the time of use
- Separation of organic chlorine compounds from lipophilic synthetic materials has been described in literature

**Type of problem:**

Investigation of possibilities to reduce 3-MCPD-FE in refined oils by absorption at surfaces of appropriated solid materials (*subsequent removal*)
## Adsorbent materials

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Type</th>
<th>Company information</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS1</td>
<td>amorphous magnesium silicate</td>
<td>&gt; 97 %</td>
</tr>
<tr>
<td>AMS2</td>
<td>amorphous magnesium silicate</td>
<td>&gt; 70 %</td>
</tr>
<tr>
<td>AMS3</td>
<td>amorphous magnesium silicate</td>
<td>&gt; 40 %</td>
</tr>
<tr>
<td>Z1</td>
<td>zeolithe</td>
<td>&lt; 20 % water (dried)</td>
</tr>
<tr>
<td>Z2</td>
<td>zeolithe</td>
<td>&lt; 1 % water (calciniert)</td>
</tr>
<tr>
<td>SO</td>
<td>silicon dioxide</td>
<td>&gt; 99.9 %</td>
</tr>
<tr>
<td>SAS</td>
<td>sodium alumosilicate</td>
<td>Perlite with citric acid</td>
</tr>
<tr>
<td>SCS</td>
<td>synthetic calcium silicate</td>
<td>47 % silicon dioxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28 % calcium oxide</td>
</tr>
<tr>
<td>SMS</td>
<td>synthetic magnesium silicate</td>
<td>65 % silicon dioxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 % magnesium oxide</td>
</tr>
</tbody>
</table>
Procedure of the treatment

Initial material: Palm oil (refined)

- Heating of 180 g palm oil at 80 °C
- Addition of 20 g adsorbent material
- 30 min stirring (magnetic stirrer with heating plate)
- Removal of adsorbent material by centrifuge (15 min, 2500g)
- Analysis of the oil
Amount of 3-MCPD-FE and related compounds in palm oil after treatment with different adsorption material

Initial content in the oil

![Graph showing the content of 3-MCPD-FE (yellow) and related compounds (red) in palm oil after treatment with different materials.](image-url)
Influence of temperature and time during treatment

Content of 3-MCPD-FE and related compounds [mg/kg] vs. Temperature [°C]

Content of 3-MCPD-FE and related compounds [mg/kg] vs. Time of treatment [min]

Initial oil

ILSI Workshop on MCPD and Glycidyl esters in Food Products, 09 -10 November 2011, Brussels
Recommendations for the production of palm oil low in 3-MCPD esters and related compounds

**In General**

- Deodorization is the most important step
- The other refining steps reduce the capability of the oils to form 3-MCPD esters and related compounds during deodorization

**Measures of mitigation**

- Optimization of palm fruit processing (short time between ripeness and processing)
- Choice of raw material with low contents of precursors
- Reducing the temperature during deodorization as low as possible
- Introduction of a washing step before refining
- Addition of diacetin, citric acid or zeolithe material during deodorisation
- Use of a two-step deodorization
- Use of a short path destillation
- Removal of glycidyl esters after refining by treatment with adsorbent materials (zeolithe or synthetic magnesium silicate) at 80 °C for 0 to 60 min with a minimum of 5 % material
Recommendations for the production of palm oil low in 3-MCPD esters and related compounds

Still open
- Definition of quality parameters for the raw material
- Optimization of the different steps
- Realization into industrial facilities

between ripeness and processing
- Choice of raw material with low contents of precursors
- Reducing the temperature during deodorization as low as possible
- Introduction of a washing step before refining
- Addition of diacetin, citric acid or zeolithe material during deodorisation
- Use of a two-step deodorization
- Use of a short-way destillation
- Removal of glycidyl esters after refining by treatment with adsorbent materials (Zeolithe or synthetic magnesium silicate) at 80 °C for 0 to 60 min with a minimum of 5 % material
Recommendations for the production of palm oil low in 3-MCPD esters and related compounds

Still open
- Definition of quality parameters for the raw material
- Optimization of the different steps
- Realization into industrial facilities

A new project has been applied at the Research Association of the German Food Industry

- Removal of glycidyl esters after refining by treatment with adsorbent materials (Zeolithe or synthetic magnesium silicate) at 80 °C for 0 to 60 min with a minimum of 5% material
Acknowledgment

Dr. J.-P. Krause, PPM
Dr. P. Fehling, PPM

Chr. Böhme, MRI
Dr. K. Vosmann, MRI
Petra Weitkamp, MRI
Andrea Schwaf, WWU Münster, MRI
N. Schumacher, FH Münster, MRI

The presented work was supported by the FEI (Research Association of the German Food Industry),
the AiF and the Ministry of Economics and Technology.
AiF-Project No.: BG 16004
I thank you for your attention